

Saturated Nitrile Solids on Titan.

R.M. Blake¹, J.R. Brookes¹, N.D. Stapleton¹, G.F. Turner¹, S.A. Boer², H.E. Maynard-Casely³,
A. Riboldi-Tunnicliffe², R.M. Williamson², D. Spagnoli¹, S.A. Moggach¹

¹*School of Molecular Sciences, The University of Western Australia, Perth, WA, Australia*

²*MX Beamlines, ANSTO Australian Synchrotron, 800 Blackburn Road, Clayton, VIC, Australia*

³*Australian Nuclear Science and Technology Organisation, Sydney, NSW, Australia*

22707733@student.uwa.edu.au

Keywords: Titan, Nitriles, Molecular Crystal

The Saturnian moon Titan has attracted significant interest over the last few decades, primarily due to its Earth-like atmospheric composition and active weather systems that create a range of surface features such as lakes, rivers, and dunes [1]. Titan has an average surface temperature of 92 K and an atmospheric surface pressure of 1.5 bar. While the atmosphere and its dynamic processes have been somewhat explored through Earth-based spectroscopic measurements and the Cassini-Huygens mission, the composition of its surface materials remains largely unknown [2]. Photochemistry in the atmosphere leads to a wide variety of chemical processes involving energised molecular nitrogen and methane reacting to form complex organic species, including nitriles. These heavy molecules eventually settle to the moon's surface where they integrate into surface processes, creating a range of molecular minerals, including co-crystals [3]. Small saturated mononitrile species have been identified on Titan, such as acetonitrile and propionitrile [4]. Larger straight chain and branched saturated mononitriles have been found in Earth-based experiments designed to mimic Titan's conditions [5]. It is possible that these types of molecules are relevant to surface minerals and surface processes on Titan.

The crystal structures of saturated mononitriles are relatively unexplored. Acetonitrile crystal structures have been extensively characterised [6] while propionitrile [7] and butanenitrile [8] each have a single known crystal structure. No crystal structures are known for other small saturated mononitriles such as pentanenitrile, isobutyronitrile and trimethylacetone. High-pressure crystallographic studies have only been conducted on acetonitrile [6]. It is possible these molecules may form crystalline solids on the surface of Titan, as both single-component structures and as co-crystals [2]. Here, we have examined single-component and co-crystals of small saturated straight-chain and branched mononitriles (up to size C₅) using high-pressure and low-temperature X-ray diffraction (XRD) techniques. XRD measurements have been complemented with periodic Density Functional Theory (DFT) calculations to determine optimum geometries, phase stabilities and lattice energies of novel crystals. A novel crystal structure of isobutyronitrile has been created at pressure (Fig. 1) and structurally examined in the range of 0.7-5 GPa. Preliminary DFT work on known nitrile crystal systems suggests that the GGA exchange-correlation functional RPBE-D3BJ models ambient-pressure nitrile crystal systems well, while the RPBE-D4 and optPBE-vdW functionals could be used to model these systems at pressure, although over-binding is observed in most high-pressure cases. Possible novel co-crystal nitrile structures will also be presented.

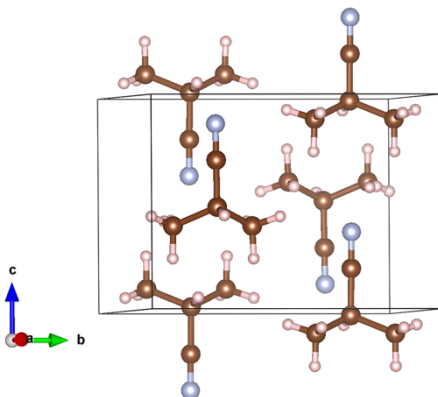


Figure 1. The crystal structure of isobutyronitrile at 0.72 GPa.

- [1] Hörst S.M. (2017). *J Geophys Res Planets.*, **122**, 432.
 [2] Maynard-Casely H.E., Cable M.L., Malaska M.J., Vu T.H., Choukroun M. & Hodyss R. (2016). *Am Mineral.*, **103**, 343.
 [3] Cable M.L., Runčevski T., Maynard-Casely H.E., Vu T.H. & Hodyss R. (2021). *Acc Chem Res.*, **54**, 3050
 [4] Cordiner M.A., Palmer M.Y., Nixon C.A., Irwin P.G.J., Teanby N.A., Charnley S.B., *et al.* (2015) *Astrophysical J Lett.*, **800**, L14.
 [5] Cable M.L., Hörst S.M., Hodyss R., Beauchamp P.M., Smith M.A., Willis P.A., (2012). *Chem Rev.*, **112**, 1882.
 [6] Olejniczak A. & Katrusiak A. (2008). *J Phys Chem B.*, **112**, 7183.
 [7] Brand H.E.A., Gu Q., Kimpton J.A., Auchettl R., & Ennis C., (2020). *J Synchrotron Radiat.*, **27**, 212.
 [8] Ishii K., Nakayama H., Koyama K., Yokoyama Y., & Ohashi Y., (1997). *B Chem Soc Jpn.*, **70**, 2085.

This work was supported by resources provided by the Pawsey Supercomputing Centre and the National Computing Infrastructure with funding from the Australian Government and the Government of Western Australia. This work was also supported by the AINSE Honours Scholarship.